SECOND QUARTERLY REPORT
11-1-66 thru 1-31-67

Prepared for
NATIONAL AERONAUTICS AND
SPACE ADMINISTRATION

Under CONTRACT NAS 7-437
GASEOUS ELECTROLYTES FOR
BATTERIES AND FUEL CELLS

S. Naiditch
Principal Investigator

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ABSTRACT

During this quarter, electrode emfs and electrolyte conductivities of one cell were measured with the electrolyte in both the liquid and dense gaseous states. Then, in order to elucidate the nature of the dense gaseous electrode interface and its differences from those of the liquid electrode interface, exploratory electrodeposition studies were initiated. It was anticipated that under conditions in which a metal and hydrogen would be co-deposited, the deposit out of the liquid state would be pock marked due to bubble formation, whereas that out of the dense gaseous state should be more continuous. The latter should show up by a more crystalline appearance, since, in the absence of a liquid skin, the hydrogen should escape without blocking portions of the surface by bubble formation. The initial data obtained this quarter appear to confirm the expectation that metallic deposits from dense gaseous electrolytes are significantly more crystalline than those from liquid electrolytes.

One cell (No. 81) was prepared with two $Pb/PbCl_2$ electrodes and two Pb(Hg) (1.77 and 0.73 mole % of lead)/$PbCl_2$ electrodes. The electrolyte was approximately 0.01 N KCl in ammonia at $-78^{o}C$, and 0.005 N at $140^{o}C$. The cell was run continuously from 20 to $140^{o}C$ and back to $115^{o}C$ over a period of eleven days. Electrode emfs were measured at intervals of 5^{o} over the entire range. Cell impedances between the two Pb electrodes were also measured throughout this range using the null sensitivity of the potentiometric voltmeter. The electrolyte impedance was measured from 140^{o} down to $120^{o}C$ using the four-probe method. Accurate and consistent impedance data were obtained with the

latter method. The electrode emfs were fairly unstable although one pair, a lead amalgam and a lead electrode, gave fairly satisfactory results over a large part of the temperature range.

Eight electrodeposition cells were built and filled and six electrodeposition experiments were run. Electrolytes were: $AgNO_3$, $Pb(NO_3)_2$, Ag_2S and CuCl. The solvent in all cases was ammonia in the liquid or dense gaseous state depending on temperature. The results on the individual cells follow.

Cell E2 contained $AgNO_3$ in NH_3. The plate from the liquid at room temperature was sponge-like whereas that deposited from the gaseous electrolyte was more crystalline in appearance with small whiskers growing radially from the wire. Also, there were large whiskers which were heavy and mossy in appearance. The current densities for the two plates were different.

The electrolyte in Cell E3 was $AgNO_3$ in ammonia. A smooth low temperature plate was obtained. The bomb itself failed during the high temperature phase of the run, terminating the experiment.

Cell E4 contained $Pb(NO_3)_2$ in ammonia. The purpose of using lead was to try to deposit a soft metal out of dense gaseous electrolyte in order to compare it with deposits of harder metals. Use of lead may not be possible. The low temperature deposit was in the form of yellowish lumps; the deposit had no metallic appearance. There was no high temperature deposit. The high temperature conductivity was unexpectedly high. It is probable that solvolysis occurred with the precipitation of $Pb(NH_2)_2$ and the formation of the "acid" ammonium nitrate, which has a high conductivity. The yellow material on the low temperature deposit may be $Pb(NH_2)_2$ or PbNH.

Cell E6 contained $AgNO_3$ in ammonia. Silver was electrodeposited at room temperature and at 142°C. The deposit at room temperature was non-uniform and gray. The deposit at 142°C was quite uniform and light in color; the surface had a sparkling appearance, in contrast to the uniformly shiny appearance usually observed on deposits from the liquids. At the tip of the platinum electrode there was a growth of whiskers or needles which were about 0.01 in. long. The gaseous electrolyte impedance was unexpectedly low.

Cell E5 was filled with Ag_2S in NH_3. Results with this cell were ambiguous. It is not clear whether enough of the material dissolved to form a useful solution. It appeared that silver was deposited at room temperature because the emf associated with the platinum electrode on which silver was reduced was increased from about 1 to about 350 mv. On standing 60 hours at room temperature, the emfs dropped to a few millivolts. After the electrodeposition, the emf of the anode decreased by about 30 millivolts and this decrease persisted after 60 hours.

Cell E10 contained CuCl in ammonia. It was hoped that monovalent copper would be soluble in ammonia and that the red color of copper would make the deposit readily visible against the platinum substrate. The deposits at -30°C from the liquid state were very dark copper red in color and had no metallic appearance. When the cell was examined after the high temperature plating, the low temperature deposit was no longer visible; neither were any high temperature deposits.

It is planned to continue the electrodeposition experiments in the next quarter in order to clarify the results of the present experiments as well as to complete this aspect of the program. In addition, we plan to adapt polarographic

techniques to our particular experimental conditions and to use this tool to unravel the source of the unexpectedly high conductivities in the dense gaseous electrolytic state which we observed in several cases.

1.0 EMF AND CONDUCTIVITY MEASUREMENTS

During this quarter, electrode emfs and electrolyte conductivities of one cell were measured; the remainder of the time was devoted to electrodeposition experiments. The emf-conductivity cell was successfully run to 140°C and was recovered intact after the experiment. In spite of severe instabilities in the electrode emfs, the conductivities were measured successfully by the four-probe method and some interesting results were obtained.

1.1 CELL 81

This cell is of a different design than those used previously and is shown in Fig. 1. Its design enables us to melt electrode materials under vacuum by heating each electrode compartment separately with a torch. This cell was prepared with two lead-amalgam/$PbCl_2$ electrodes and two solid lead/$PbCl_2$ electrodes, in order to further evaluate the behavior of solid lead/$PbCl_2$ electrodes. The electrode compositions were as follows:

Electrode	A	B	C	D
Mole % Lead	1.77%	100%	100%	0.73%

A phase transition should occur in electrode A at about 25 - 30°C. Above this temperature, each of the metallic portions of the electrodes should be single phase. About 10 mg of $PbCl_2$ was added to each of the amalgam electrodes while about 30 mg of $PbCl_2$ was added to each of the solid lead electrodes. The solid electrodes were formed by melting a mixture of granular lead and $PbCl_2$ under vacuum. It was hoped that an intimate contact could be produced between the two materials in this manner.

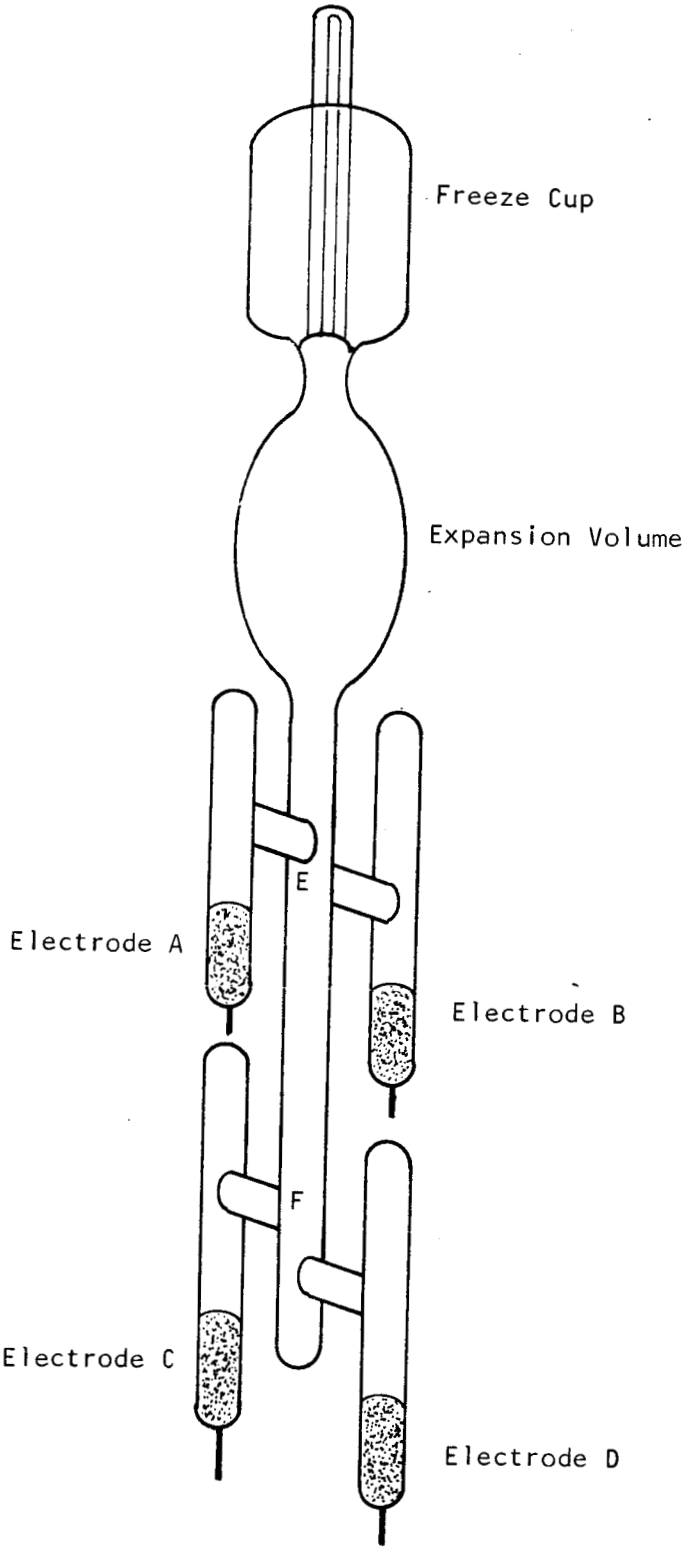


Fig. 1 Cell for Electrode Studies - approximately full size.

Unfortunately, most or all of the $PbCl_2$ became separated from the lead in electrode C during fusion. The addition of $PbCl_2$ to the other electrodes appeared satisfactory. The cell was filled to half of its volume with a 0.01 normal solution of KCl in ammonia at -78°C.

This cell was run continuously from room temperature to 140°C and back to 115°C over a period of 11 days. The cell was removed intact from the bomb. Measurements of electrode emfs were taken at intervals of 5°C over the complete range. Using the nulling sensitivity of the potentiometric voltmeter, the cell impedance between electrodes B and C was obtained, as described in the last quarterly report. Using the four-probe method, the electrolyte impedance was obtained, using A and D as working electrodes and B and C as measuring electrodes. This was done during the decreasing temperature portion of the run from 140° to 120°C. This impedance is not between electrodes B and C but between the points on the central tube of the cell where the tubulations from these electrodes join the central tube, namely points E and F on Fig. 1.

The results are summarized in Table 1. The electrode emfs are fairly unstable (Fig. 2, 3 and 4), especially those involving electrode C. The combination DB is the best behaved indicating that the solid lead electrode B may be fairly stable. As can be seen from Table 1, the emf between the supposedly identical electrodes B and C was appreciably different from zero. An attempt to reform electrode C by passing a current between electrodes A and C at 140°C in order to form a $PbCl_2$ layer on C produced no significant change in the electrode emfs. The cell impedance between electrodes B and C

TABLE 1

TIME HOURS	TEMP °C	ELECTRODE EMF IN MV				CELL IMPEDANCE BC IN OHMS
		DA	DB	DC	BC	
0	22	-10.6	+ 1.6	-32.0	-25.3	5.62×10^{5}
87.25	19	+ 5.4	- 0.6	+ 2.6	+ 3.4	1.11×10^{5}
95.17	21	+ 5.9	+ 1.1	+ 4.3	+ 3.1	1.11×10^{5}
120.33	21	+ 5.9	+ 2.6	+ 5.3	+ 2.7	9.99×10^{4}
157.75	21	+ 6.0	+ 4.3	+ 6.8	+ 2.5	9.99×10^{4}
159.33	27	+ 4.6	+ 2.5	-52.4	-53.6	6.14×10^{6}
161.00	33	+ 4.2	+ 0.1	+11	+11.3	6.69×10^{6}
162.50	39	+ 5.2	+ 1.2	+23	+22.6	6.14×10^{6}
164.00	44	+ 9.2	+16.9	+22.8	+ 5.5	2.12×10^{5}
165.00	50	+15	+16.3	+15.5	- 1.3	2.50×10^{5}
166.75	54	+15.9	+21.9	+18.8	- 3.5	4.92×10^{5}
176.50	60	+13.5	+23.8	+20.5	- 3.3	8.52×10^{5}
178.33	66	+13.5	+25.0	+21.5	- 3.5	8.52×10^{5}
180.00	71	+14.1	+26.0	+22.5	- 3.5	9.61×10^{5}
181.25	75	+15.0	+27.2	+23.5	- 3.8	8.52×10^{5}
183.67	80	+16.3	+29.1	+25.8	- 3.7	8.52×10^{5}
186.00	85	+17.2	+30.3	-26.7	- 3.9	8.52×10^{5}
187.25	89	+18.6	+31.0	+27.8	- 3.3	1.00×10^{6}
204.83	93	+19.1	+32.3	+18.1	-14.2	1.22×10^{6}
206.33	99	+19.1	+34.0	+20.0	-14.3	1.50×10^{6}
207.08	105	+17.3	+36.5	+20.0	-16.5	1.63×10^{6}
208.83	110	+16.5	+37.9	+20.0	-18.1	2.45×10^{6}
211.67	115	+16.5	+37.4	+20.5	-17.0	4.00×10^{6}
214.33	120	+16.5	+33.8	+25.5	- 8.4	7.33×10^{6}
229.42	123	+ 9.7	+32.4	+18.4	-15.4	4.00×10^{6}
230.83	128	+ 9.6	+30.4	+18.6	-12.3	4.26×10^{6}
232.33	136	+ 9.5	+25.4	+19.6	- 6.7	4.26×10^{6}
234.00	140	+ 9.3	+26.5	+20.7	- 5.8	4.00×10^{6}
241.50	140	+10.3	+29.4	+22.4	- 7.6	3.76×10^{6}
253.83	140	+ 8.5	+32.1	+21.2	-11.2	3.76×10^{6}
257.17	140	+ 8.3	+32.2	+21.1	-11.7	3.54×10^{6}
257.83	140	+ 8.9	+32.3	+21.1	-11.6	3.76×10^{6}
258.00	140	+ 9.4	+32.3	+20.4	-12.0	3.76×10^{6}
259.17	140	+ 8.9	+32.5	+21.7	-11.1	3.54×10^{6}
260.33	135	+ 9.4	+32.6	+20.8	-12.1	3.54×10^{6}
262.00	130	+ 9.6	+32.6	+20.2	-12.4	3.54×10^{6}
263.17	125	+ 9.9	+32.8	+20.6	-12.6	3.34×10^{6}
265.00	120	+14.1	+40.6	+22.6	-18.0	2.84×10^{6}

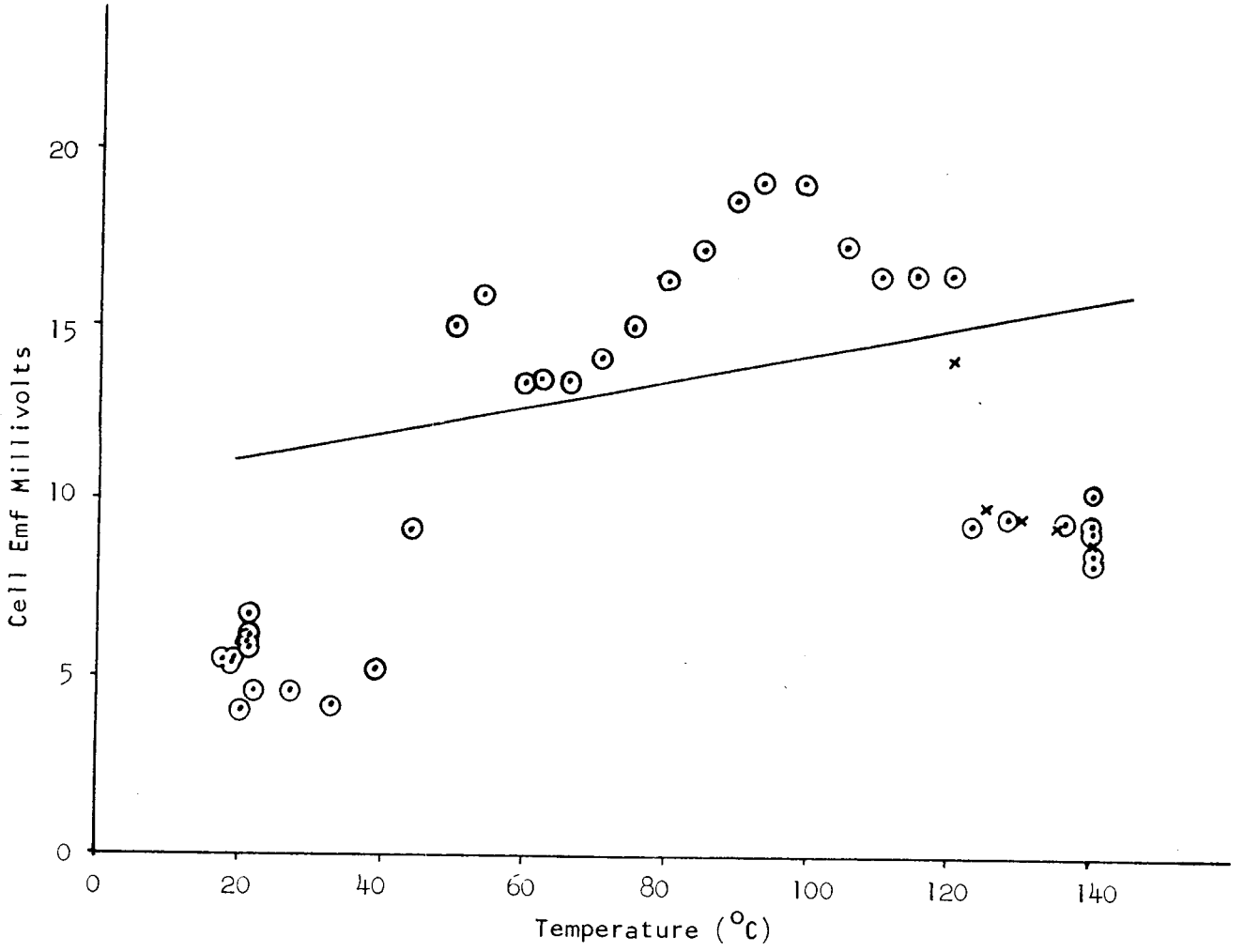


Fig. 2 Cell Emf DA vs Temperature

⊙ Increasing Temperature

× Decreasing Temperature

Solid Line - Predicted emf for a simple solution of Pb in Hg

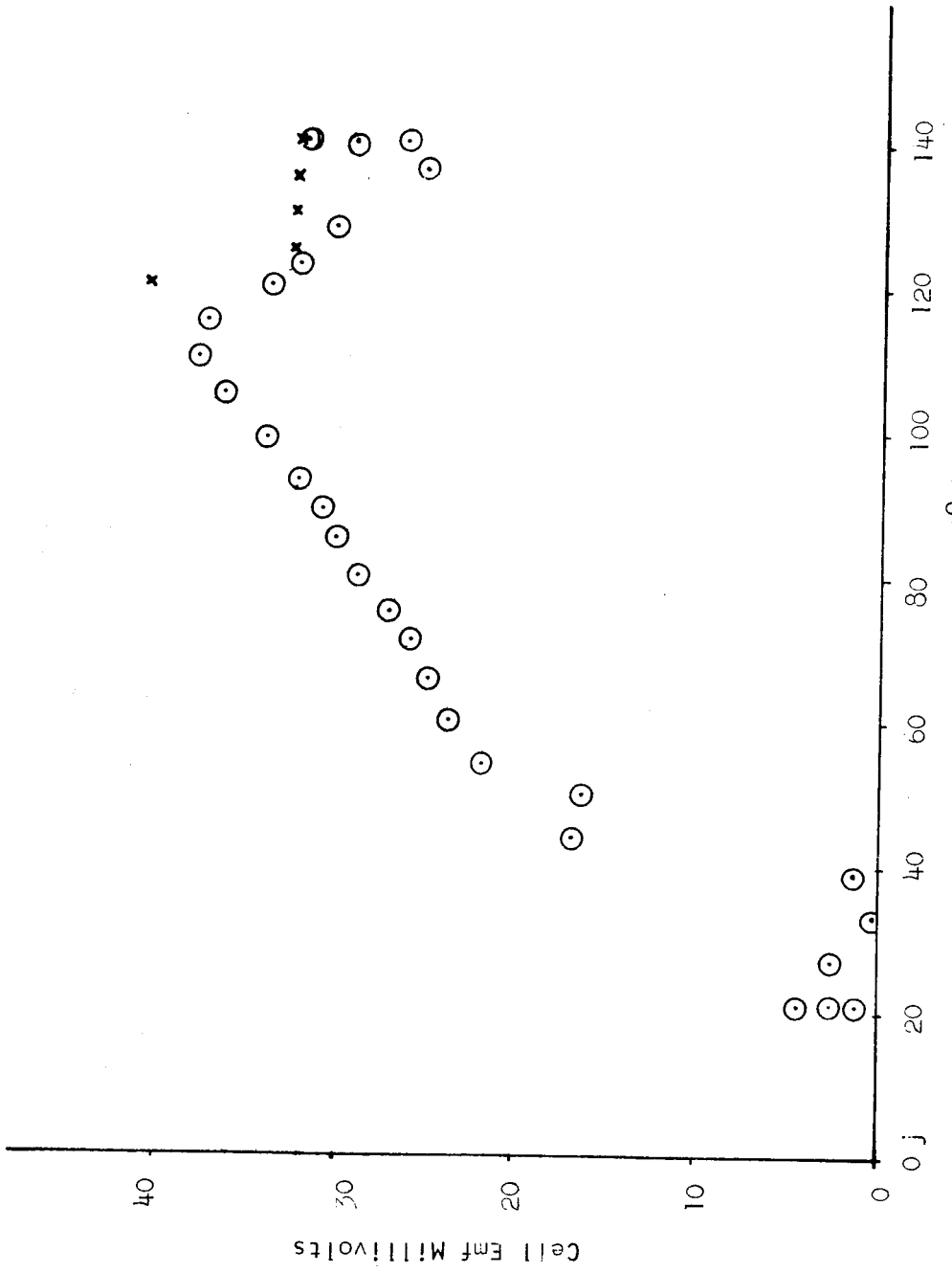


Fig. 3 Cell Emf DB vs Temperature

⊙ Increasing Temperature

× Decreasing Temperature

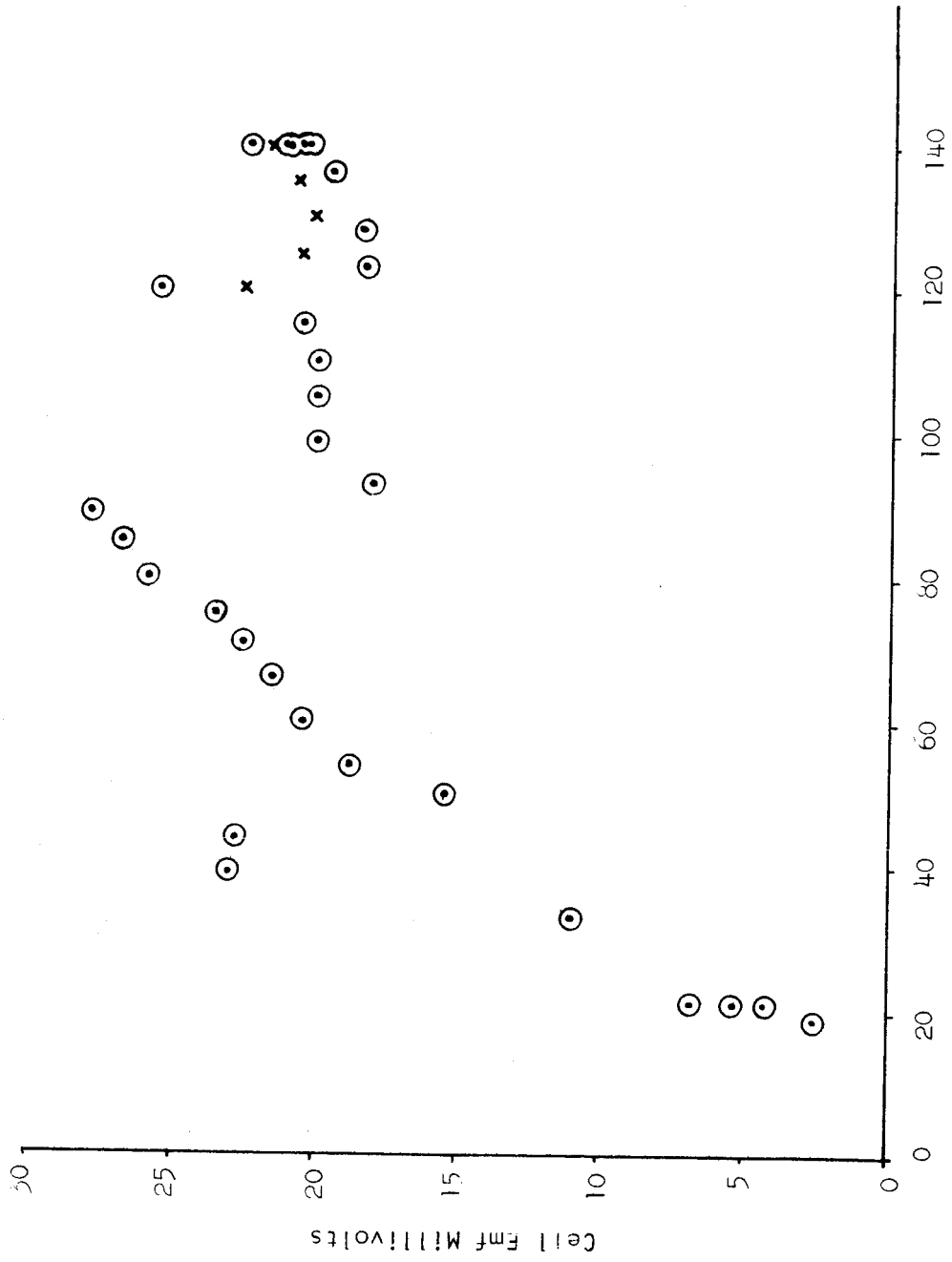


Fig. 4 Cell Emf DC vs Temperature

⊙ Increasing Temperature

× Decreasing Temperature

as determined from null sensitivity is shown in Fig. 5. The very wide scatter of the measured points indicates malfunction of at least one of the electrodes. Such electrode malfunction should have the effect of increasing the cell impedance above its normal value. The lower points on Fig. 5 should therefore be the most meaningful and the line drawn through them has a quite reasonable shape. The "knee" in this line occurs at a temperature of 127°C and indicates the point where the cell is completely filled with a single phase liquid electrolyte. At temperatures above this point, the electrolyte density is constant and the impedance does not change much with changing temperature. At temperatures below this point, the dielectric constant of the electrolyte decreases with increasing temperature so that the cell impedance is an increasing function of temperature.

This feature is shown more clearly in Fig. 6 of the four-probe measurements of the electrolyte impedance between the points E and F (cf. Fig. 1). These measurements were obtained by passing a current between electrodes D and A while measuring the voltage between electrodes B and C. Fig. 6 shows some examples of the voltage BC vs the current AD. Such plots were made at each of the temperature points investigated. The v vs i plots were all quite linear, the slope being the electrolyte impedance between points E and F. This impedance is plotted vs temperature in Fig. 7. This plot has a "knee" at 126.5°C, in agreement with the null sensitivity measurements, and, as before, the impedance is an increasing function of temperature below this point. It is also seen that above this point, the impedance is a decreasing function of temperature, which is encouraging from the point of view of a

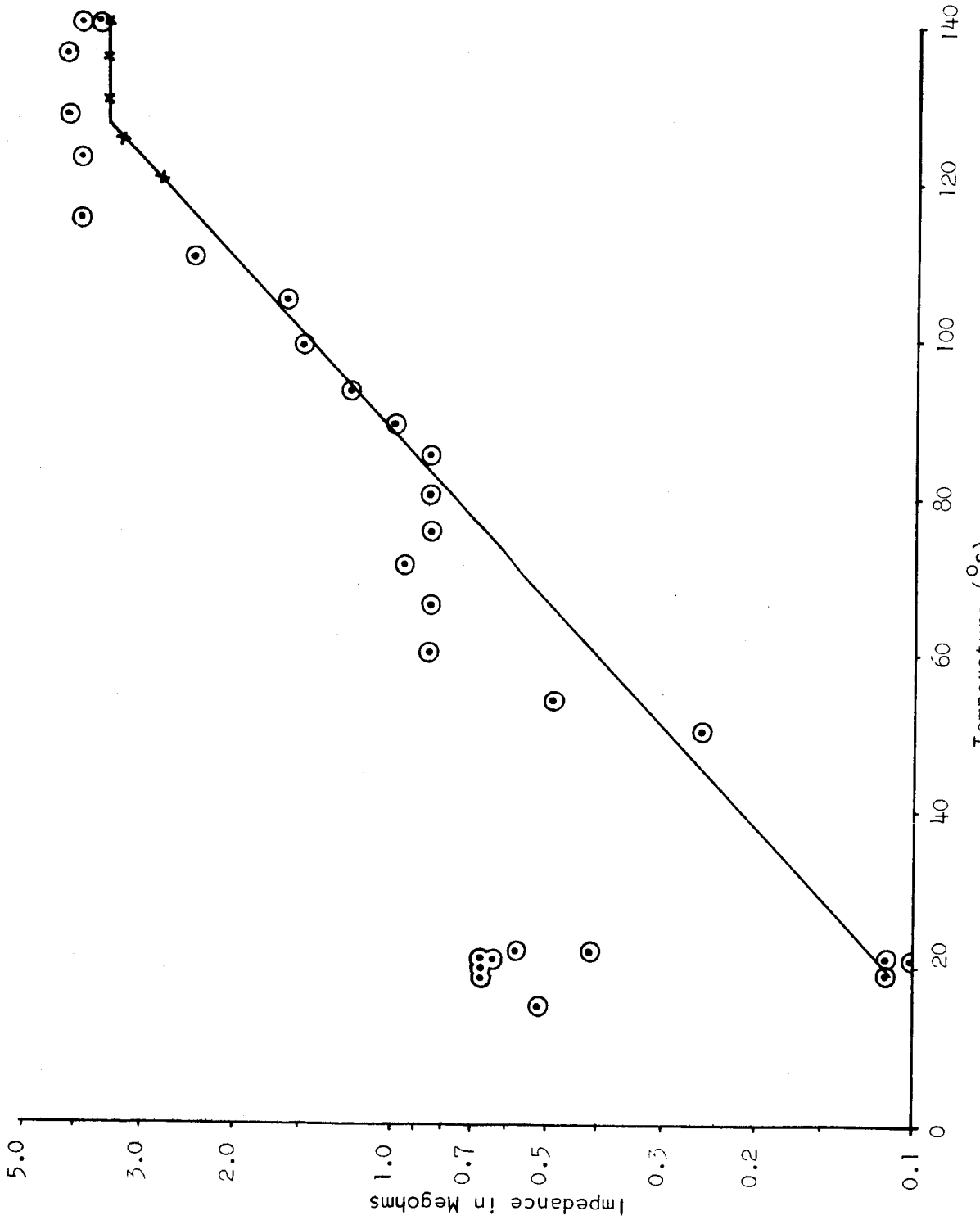
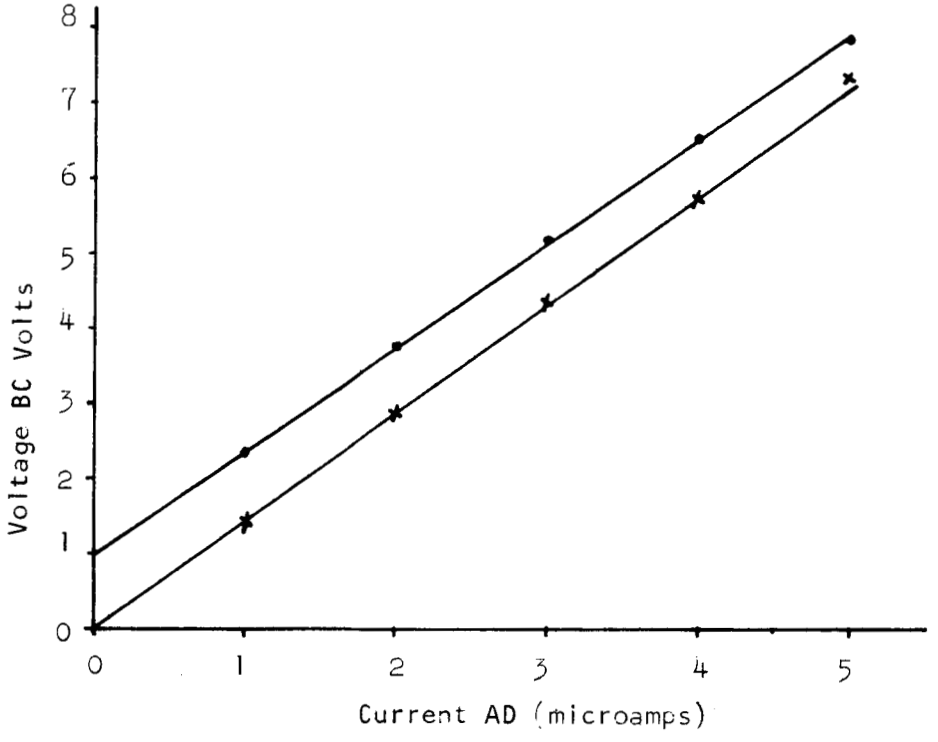


Fig. 5 Cell Impedance BC by Null Sensitivity Method
⊙ Increasing Temperature
X Decreasing Temperature



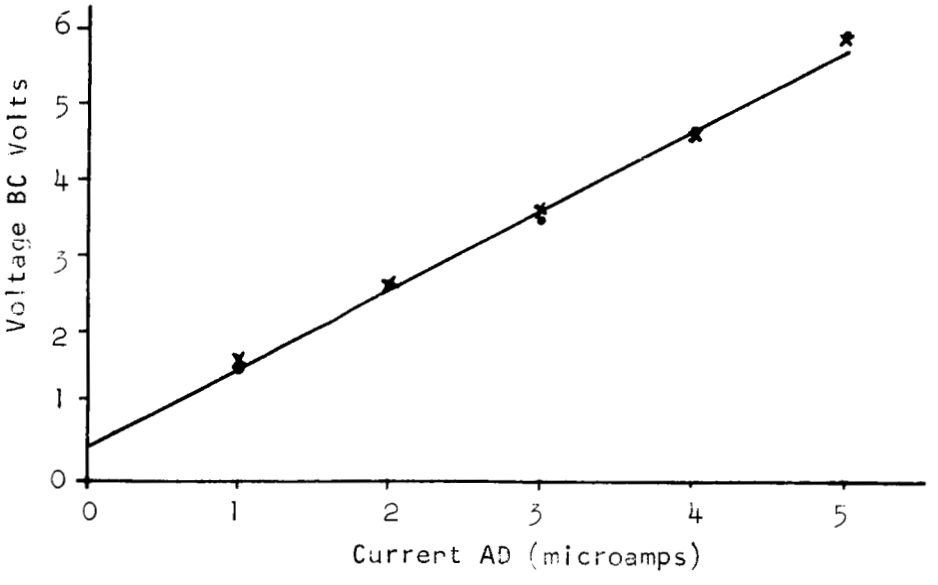


Fig. 6 Voltage Between Electrodes BC vs Current Between Electrodes AD

• Current in A^+D^- Direction

× Current in A^-D^+ Direction

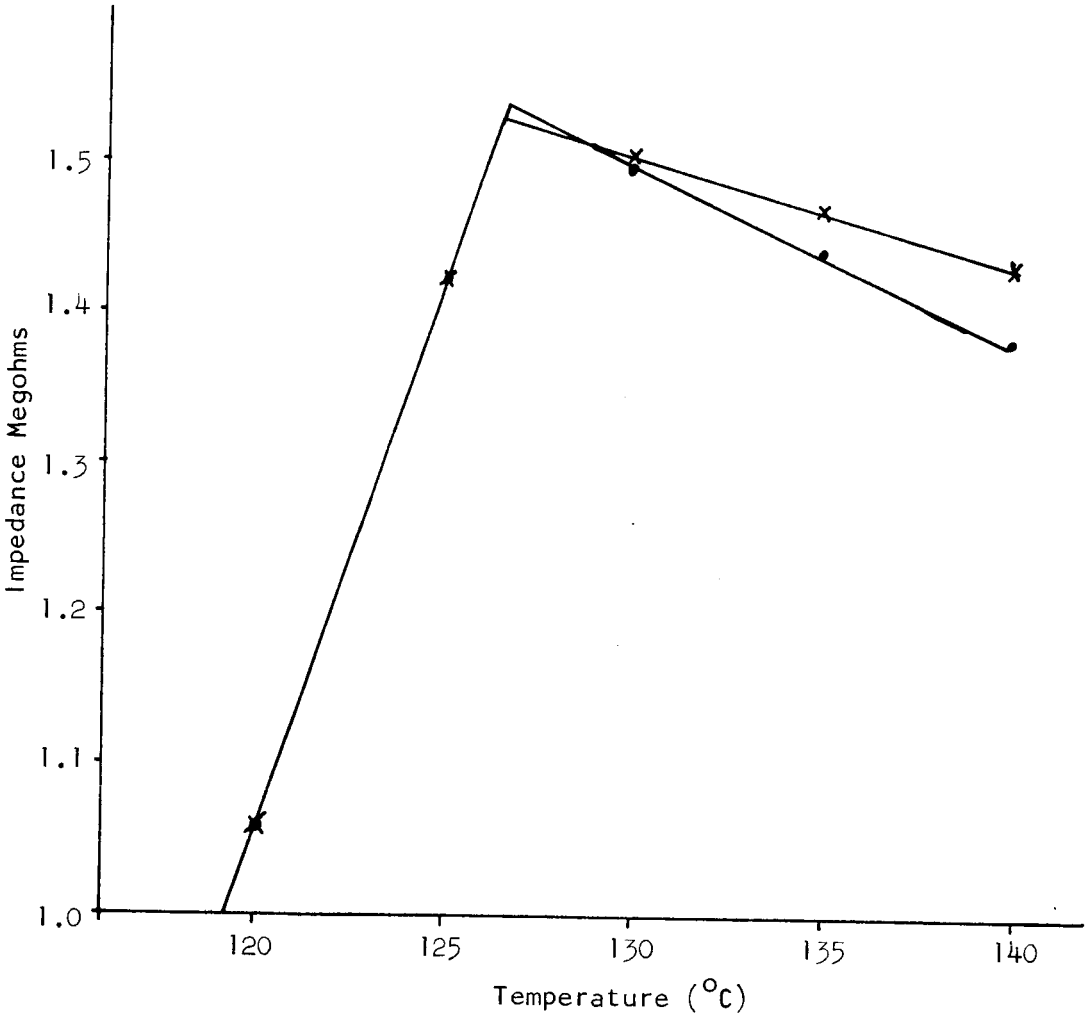


Fig. 7 Electrolyte Impedance EF vs Temperature by Four-Probe Method

• Current in E^+F^- Direction (A^+D^-)

× Current in E^-F^+ Direction (A^-D^+)

possible gas phase battery. The impedance between E and F is less than that between B and C by a factor of about 2.5, as is expected from the cell geometry. An unexpected feature of the v vs i plots (Fig. 6) is that the lines corresponding to the opposite direction of current are displaced in voltage for the higher temperature points. This displacement disappears for the lower temperature points, so that the lines for the two current directions coincide for temperatures below the cell filling point and are displaced by increasing amount as the temperature is increased above this point. The reason for this behavior has not yet been determined.

2.0 ELECTRODEPOSITION EXPERIMENTS

2.1 DISCUSSION

Before turning to the experimental data, we shall discuss the objectives and our conjectures concerning this aspect of the program. Briefly, in the earlier phases of the program we have shown that dense gaseous electrolytic solutions do not affect the thermodynamic or equilibrium properties of amalgam concentration cells. In a sense this was a confirmation of an expectation; nonetheless, since this is the first time such studies have been undertaken, it is essential to establish the basic behavior of the system.

In this newer phase of the program we are concerned with finding electrochemical properties that are affected by the state of the electrolyte. One promising aspect which has never been examined is the study of the properties of the electrolyte-electrode interface. The present series of experiments is designed to provide an exploratory survey of steady state interfacial phenomena using a simple but effective technique, that of electrodeposition. Our conjectures guiding these experiments will now be discussed.

Principal differences in behavior of cells using liquid versus gaseous electrolytes should include: (1) the presence versus absence of a liquid skin at the interface; and (2) the invariance at a given temperature versus easy variation of dielectric constant of the solvent as well as degree of solvation of the solute. The tool we are using for this exploration is electrodeposition of a metal. Experiments are being run by carrying out the deposition from the liquid state at various temperatures and from the dense gaseous state at elevated temperatures. In this way side effects, such as

those produced by trace impurities, may be similar for both types of deposits for a given cell.

The parameters to be varied include current density, pH, the per cent filling (which leads to variation of dielectric constant and degree of solvation in the dense gaseous solutions), and the use of soft versus hard metals. By varying the pH of the solution (the acid is, of course, NH_4^+), we can influence the ratio of hydrogen liberated to metal deposited. In the case of deposition from the liquid state, as molecular hydrogen desorbs from the surface, it will be constrained to the neighborhood of the surface by the surface tension of the liquid. Thus bubbles form and persist in the neighborhood of the surface. The electrodeposit from the liquid state under unfavorable conditions can then look like a porous or pock-marked deposit. Decreasing the pH by the addition of NH_4NO_3 will increase the amount of hydrogen evolution, and therefore the bubble effect.

Turning now to electrodeposition from the dense gaseous state, we immediately note one very important change. As the molecular hydrogen desorbs from the surface, it is not constrained to stay in the neighborhood of the surface, but can diffuse in any direction in the electrolytic gas. A small amount may diffuse back to the surface, but the majority will leave permanently. In no case will there be a mechanical obstruction such as a bubble which prevents electrodeposition in its neighborhood. Thus, in the case of the gaseous electrodeposition, one might expect a greater coherency of deposition, which may manifest itself in a more crystalline deposit, under favorable conditions it may be possible to deposit single crystals or whiskers.

2.2 SUMMARY

During the past quarter, eight electrodeposition cells (E3 to E10) were built and filled and six electrodeposition experiments were run. The cells were all of the type shown in figure 8 and differed in the length of the platinum electrode and in the electrolyte. They are summarized in the following table.

Cell	Electrolyte	Electrodes
E3	$AgNO_3$	Four 2"x0.016" Pt wires
E4	$Pb(NO_3)_2$	Four 1.2"x0.016" Pt wires
E5	Ag_2S	Four 1.2"x0.016" Pt wires
E6	$AgNO_3$	Four 1.2"x0.016" Pt wires
E7	CuCl	Six 1.2"x0.016" Pt wires
E8	$AgNO_3$	Six 1.2"x0.016" Pt wires
E9	$AgNO_3$	One 2"x0.016" Pt wire and five 0.016" diam. Pt surfaces
E10	CuCl	One 2"x0.016" Pt wire and five 0.016" diam. Pt surfaces

Of these, Cell E7 broke during filling and Cels E8 and E9 were not yet run. The remaining cells were run with varying degrees of success. In addition, Cell E2, which had been filled during the previous quarter, was run. The reports on the individual experiments follow.

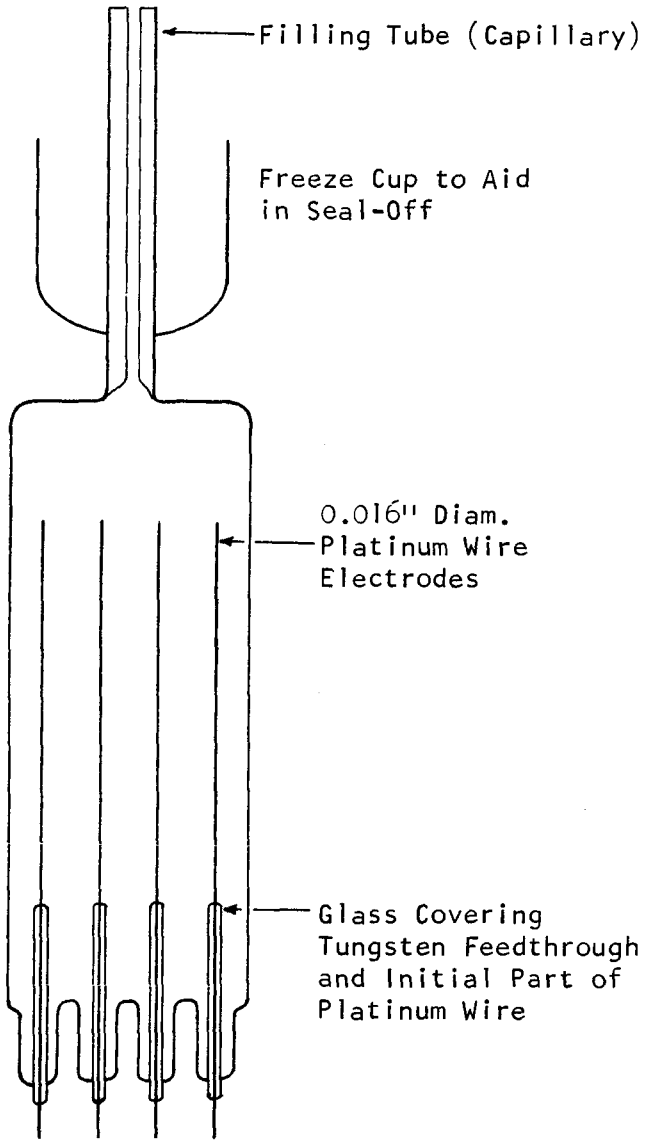


Figure 8. ELECTROPLATING CELL

In some cells two additional electrodes have been brought in through the top of the cell.

In some cells the cathodes have been cut off flush with the feedthrough glass.

2.3 CELL E2

A cell consisting of a 30 mm O.D. glass cylinder about 72 mm long and containing four parallel 2" x 0.016" diameter platinum wire electrodes was filled with 0.1593 gm of $AgNO_3$ in 20 cc of NH_3 at -78°C. One electrode was chosen as the anode, two as cathodes and the remaining one as a reference electrode. One cathode was plated with silver at room temperature so that the electrolyte was in the liquid state and subsequently the other was plated at a temperature well above the critical temperature of ammonia. The cell impedance during the gaseous plating was so high that the cell current was only a fraction of that used for the liquid plating, even though a much higher voltage was used. The experimental conditions were as follows:

Electrolyte State	Temp. °C	Approx. Cell Pres. Atm.	Cell Volts	Current ma.	Time Sec.	Charge Faradays
Liquid	21	9	4.5	47	100	4.7×10^{-5}
Gas	150	230	200	5.2	500	2.7×10^{-5}

Small diameter wires were used as electrodes in order to obtain high current densities so that depletion effects at the electrode surfaces would be amplified. The deposits obtained were therefore not smooth and uniform, as had been obtained earlier at a lower current density. The liquid phase plating was in the form of a heavy, mossy, sponge-like, somewhat cratered or pock marked deposit on the cathode. The gas phase deposit was more crystalline in appearance with small whiskers growing radially from the wire. Larger whiskers were heavy and mossy in appearance and in places would merge to form a mossy deposit. Smaller whiskers appeared more like small crystals. This is in agreement with the expected behavior in that the spongy, pockmarked

appearance of the liquid phase plating is probably a result of the formation of hydrogen bubbles. Such bubbles would inhibit the formation of crystals such as appeared in the gas phase plating. The result is not conclusive since the current densities were so different.

2.4 CELL E3

This cell (whose volume was approximately 40 cc) was filled with 0.1600 gm of $AgNO_3$ in about 20 cc of NH_3 at -78°C. The cell was placed in the bomb and allowed to warm. At a temperature of 16°C a current of 5.3 ma was run between the anode and one cathode for 100 seconds. The total charge was thus about 5.5×10^{-6} faradays, approximately one-fifth of that used in the previous electrodeposition experiment. The voltage between this cathode and the anode during plating was 1 volt, while the voltage between the reference electrode and the cathode was 0.5 volts. The cell was then heated to 145°C and subjected to an external pressure of 240 atm. At this point, before electrodeposition could be tried, the thermocouple blew out of its seal in the bomb head and pressure was lost, allowing the cell to burst. This was the first time the small bomb had been used since the beginning of the program, and it is believed that the thermocouple is presently installed so that the trouble cannot occur again.

The electroplate obtained at 16°C was much smoother than was obtained in the previous experiment (E-2) where a much higher current density and total charge were used. The deposit appeared as a thin, fairly uniform, coating of silver on the first cathode. The coating is somewhat rough, having lumps or hills rising from a smooth background. There are some black stains on the deposit, possibly from decomposed $AgNO_3$ left there after the cell burst.

2.5 CELL E4

This cell (of 40 cc volume) was filled with 0.2698 gm of $Pb(NO_3)_2$ in about 20 cc of NH_3 at -78°C. The solution appeared slightly cloudy, indicating either incomplete dissolution, or solvolysis with the formation of a slightly soluble amide. Disproportionation (to form $Pb^o + Pb^{++}$) does not appear to be likely since no elementary lead was observed.

Currents were passed through the cell at room temperature and at a temperature above the critical point. The conductivity at 142°C was higher than expected. The experimental conditions were as follows:

Temp. °C	Cell Volts	Current ma.	Time Sec.	Charge Faradays
20	2.4	5.3	126	6.7×10^{-6}
142	55	5.3	126	6.7×10^{-6}

The deposit at 20°C on the low temperature cathode was in the form of yellowish lumps on a dull, dark Pt background. The deposit had no metallic appearance. There were numerous large yellow lumps with spaces between occupied by many small yellow lumps.

The high temperature cathode had turned blackish, the black flim being continous. This black film was insoluble in concentrated nitric acid, which would indicate that it may have been finely divided platinum produced by reduction of NH_4^+ on that surface, rather than lead which is soluble in nitric acid.

One possible interpretation of these facts is that solvolysis may occur.

$$Pb^{++}(NO_3)_2^- + 2NH_3 = Pb(NH_2)_2 + 2NH_4^+NO_3^-$$

At higher temperatures the solubility of lead amide may be considerably lower than at room temperature thus driving the reaction toward completion. At high temperatures, this would lead to formation of ammonium nitrate which would account for the unexpectedly high observed conductivity and absence of lead deposition. The lead amide might well be yellow in appearance and might also be present as PbNH under the conditions of formation. Finally, as lead amide is formed with increasing temperature, it would start precipitating from solution. Possibly it would deposit preferentially on the lead coating and this might account for the yellow lumps deposited in that region.

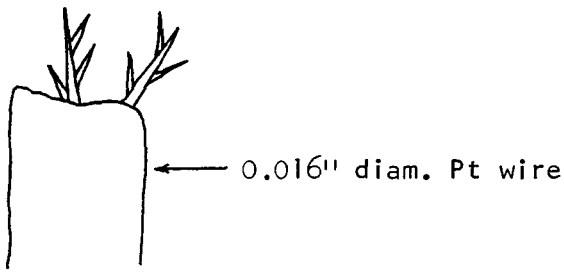
2.6 CELL E6

This cell (with a volume of 40 cc) was filled with 0.1733 gm of $AgNO_3$ in about 20 cc of NH_3 at -78°C. Electrodepositions were made at room temperature and at a temperature above the critical point of NH_3. The experimental conditions were as follows:

Temp. °C	Cell Volts	Current ma.	Time Sec.	Charge Faradays
18	1.65	5.7	120	7.1×10^{-6}
142	8.2	5.7	120	7.1×10^{-6}

The silver deposit at 18°C was nonuniform and a bit dirty in appearance. The deposit was in the form of gray lumps on a dull black background. It is not known why this deposit is less clean and less uniform than that obtained with Cell E3 under similar conditions.

The silver deposit at 142°C was quite uniform and very clean in appearance. Although no roughness was visible over most of the deposit, the surface had a sparkly appearance rather than a uniformly shiny appearance. The most interesting feature was the growth of whiskers or needles about 0.01" long on the tip of the Pt wire electrode. The appearance of these is illustrated in the following sketch.



This indicates that single crystals of Ag were grown from the gaseous electrolyte.

Another interesting result from this cell was that the cell voltage during plating at 142°C was only five times greater than at 18°C. This indicates an increase of electrolyte impedance by only a factor of 5 while going from 18° to 142°C. On the previous gaseous electrodeposition (E2), the cell impedance increased by a factor of 400. This discrepancy might be due to a greater electrolyte density in the cell E6 due to a greater fractional filling with NH_3. The approximate concentrations of gaseous ammonia in the two cells are 21 and 24 mole/liter. The difference appears to be too small to account for the difference in cell impedance. However, if the ammonia densities are in the right region, then the dielectric constant increases approximately exponentially with ammonia concentration. Since the dielectric constant of dense gaseous ammonia has never been measured as a function of temperature and concentration, one cannot draw a definite conclusion on this point at this time.

2.7 CELL E5

This cell (with a volume of 40 cc) was filled with 0.1531 gm of Ag_2S in 20 cc of NH_3 at -78°C. This cell was intended both for electrodeposition and to see whether $S^=$ could be oxidized in situ to form a useful electrode in ammonia. Most of the Ag_2S remained undissolved in the bottom of the cell. The four Pt wire electrodes were designated A, B, C and D. The cell was loaded in the large bomb, allowed to warm to room temperature, and emf measurements were made on the six electrode pairs. A current of 0.5 ma was run for 120 seconds between the electrodes A and D with the polarity A^+D^-. Thus D had a deposit of silver and A may have had sulfur (in a valence state higher than sulfide). The cell voltage required was 33 volts. Emf measurements were again made on the six electrode pairs. The emf measurements were repeated after 60 hours. The cell was then heated and emf measurements were made at 90°C. The cell was then raised to 145°C but was found to be open circuited and apparently broken so that no further experiments could be tried. The emf measurements were as follows:

Approx. Time Hrs.	Temp. °C	Electrode Emfs in mv AB	AC	AD	CD	BD	BC	Notes
0	20	-5.1	-0.8	+0.7	+1.3	+5.6	+4.0	Before charging
1	20	-35	-26	+348	+355	+373	+9	Just after charging
60	20	-38.8	-40.7	-35.9	+2.7	+2.3	-1.1	(After standing (~ 60 hours
61	90	0	+4.9	+1.4	-6	-2	+4.3	After heating

After the electrolysis, the voltages on all pairs except BC were not stable and were either dropping or rising rapidly. BC was steady. After the run,

when the cell was removed from the bomb and the electrode surfaces examined with a microscope, no deposits were visible.

The results of this run are ambiguous. The silver that was deposited (as evidenced by the increase in emf of electrode D by about 350 mv) appeared to redissolve at room temperature, whereas, the oxidized sulfide (decrease in emf of electrode A of about 30 mv) appeared to persist.

2.8 CELL E10

This cell (with a volume of $\sim$ 40 cc) was filled with 0.1096 gm of CuCl in 20 cc of NH_3 at -78°C. It was hoped that the red color of copper would make the deposit more clearly visible against the silvery platinum substrate. Unfortunately, the CuCl cell with long electrodes (E7) was broken during the filling process. Cell E10 had the cathode wires cut off flush with the glass which covered the feedthrough wire for a distance of $\sim$ 3/4" into the cell. A 0.016" diameter surface of Pt was thus exposed for the cathode surface. The CuCl did not completely dissolve in the ammonia but turned from its normal yellow color to pale blue on exposure to ammonia. The liquid in the cell had a blue color indicating that some of the salt had gone into solution. The valence state of the material in solution was not established.

There were six electrodes in this cell, one anode and five cathodes. Two of the cathodes were used for low temperature electrodeposition prior to placing the cell in the bomb while the remaining three were used for high temperature electrodeposition. The two low temperature cathodes were

designated Gn and Gy while the anode was designated A and the three high temperature cathodes were B, C and D. The experimental conditions were as follows.

Cathode	Temp. °C	Cell Volts	Current ma.	Time Sec.	Charge Faradays
Gn	-30	2	0.2	3600	7.5×10^{-6}
Gy	-30	5	2.2	840	1.9×10^{-5}
B	97	375	0.04	900	3.7×10^{-7}
C	142	375	0.037	3600	1.37×10^{-6}
D	115	375	0.033	900	3.1×10^{-7}

The low temperature deposits were examined visually before the high temperature plating was attempted. The deposits were seen to be in the form of approximately spherical growths on each cathode, the one on Gn being about 1.5 mm diam. while the one on Gy was about 4 mm diam. The deposits were very dark coppery red in color and had no metallic appearance. When the cell was removed from the bomb after the high temperature plating, the low temperature deposits were no longer visible and no high temperature deposits were visible. Inspection of the electrodes with a microscope showed discoloration but no apparent deposit, although it was difficult to be certain on so small an electrode surface.

The disappearance of the low temperature deposits after heating and the apparent absence of high temperature deposits suggests that the deposits formed may be soluble at high temperatures. An interesting feature of the low temperature deposits is their large volume, indicating a low density.

Assuming that solid copper of density 8.96 is the substance deposited, a spherical deposit of 1.9×10^{-5} Faradays of Cu^{+} should have a diameter of 0.65 mm or only 1/6 of the diameter of the deposit observed on Gy. The density of the deposit on Gy is therefore only 1/200 of the density of copper assuming a monovalent cation. Similarly, the density of the deposit on Gn is 1/40 the density of copper. The difference between the two is probably due to a factor of 10 in current density. A possible explanation is that the deposits formed at low temperature and high current density are very porous copper deposits which either dissolved or disintegrated during the course of the high temperature experiments. It is planned to repeat the high temperature CuCl experiments using longer electrodes and to check the solubility of copper in ammonia at high temperatures.

3.0 FUTURE PLANS

During the next quarter it is planned to continue the electrodeposition experiments and hopefully bring them to a conclusion. It is also planned to try some conductivity experiments above and below the critical point using a silver nitrate in ammonia electrolyte and silver electrodes. Since the silver, silver nitrate, ammonia system seems so well behaved in the electrodeposition experiments, it is hoped that meaningful conductivity measurements can be made as a function of temperature, concentration, and density. Finally, it is planned to initiate experiments in polarography using the dropping mercury electrode technique. These would be the first gas phase polarography measurements and should permit identification of the gaseous ions, e.g. in the case of the lead experiments.